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(72) Inventors: VALINT, Paul, L., Jr. ; 1 Farm Field Lane, Pittsford, NY 14534 (US). MCGEE, Joseph, A. ; 125 Terrace View Road, Dewitt, NY 13214 (US).

(74) Agents: POLYN, Denis, A. et al.; Bausch & Lomb Incorporated, Patent Law Department, One Lincoln First Square, P.O. Box 54, Rochester, NY 14601-0054 (US).

(54) Title: SURFACE-ACTIVE MACROMONOMERS

(57) Abstract

A new class of polymerizable surfactants, useful for modifying the surfaces of polymeric objects, which are described by the formula: $DC[A_xB_y]$ wherein A is at least one ethylenically unsaturated hydrophilic monomer, B is at least one ethylenically unsaturated hydrophobic monomer, C is a functional chain transfer agent, D is an ethylenically unsaturated end group, y is within the range from about 0.1 to about 0.9, and x + y = 1. Also disclosed are random copolymer precursors of such polymerizable surfactants.

SURFACE-ACTIVE MACROMONOMERS

BACKGROUND OF THE INVENTION

The present invention is directed to materials useful for modifying the surfaces of solid materials and more particularly to polymerizable surfactants.

Surface structure and composition determine many of the physical properties and ultimate uses of solid materials. Characteristics such as wetting, friction, electrostatic charging, and adhesion are largely influenced by surface characteristics. Of particular concern are the effects of such surface characteristics on biocompatibility. The alteration of surface characteristics is therefore of special significance in biotechnical applications. Improved methods are accordingly sought for modifying solid surfaces, particularly the surfaces of polymeric objects.

Random, grafted, polymerized surfactants have been used to modify the surfaces of hydrophobic polymers by the adsorption of the surfactant onto the surfaces of polymeric objects from an aqueous dispersion. Lee, J. H., _Interactions of PEO-Containing Polymeric Surfactants With Hydrophobic Surfaces_, The University of Utah (1988)(hereinafter "Lee"). Lee--particularly concerned with reducing the absorption of blood plasma proteins on hydrophobic surfaces--teaches the synthesis of polymeric surfactants by random free radical copolymerization of a hydrophobic methacrylate (hexyl methacrylate or lauryl methacrylate), a

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hydrophilic methacrylate (polyethylene oxide
methacrylate), and methyl methacrylate.

Akashi, M., et al., "Graft Copolymers Having
Hydrophobic Backbone and Hydrophilic Branches. IV. A
Copolymerization Study of Water-Soluble
Oligovinylpyrrolidone Macromonomers," J. Polymer
Sci.: Part A: Polymer Chemistry, Vol. 27, pp. 3521-
3530 (1989)(hereinafter "Akashi") teaches
amphiphiles prepared by random free radical
copolymerization of carboxyl group-terminated
oligovinylpyrrolidone with methyl methacrylate or
styrene. Syntheses of vinylphenyl-terminated and
methacryloyl-terminated oligovinylpyrrolidone
macromonomers are described.

Polymerizable surfactants have been used to
modify the properties of polymers in aqueous
solution. For example, Schulz, et al., "Copolymers
of Acrylamide and Surfactant Macromonomers:
Synthesis and Solution Properties," Polymer, Vol.
28, pp. 2110-2115 (Nov., 1987)(hereinafter "Schulz")
describes macromonomer surfactants wherein the
surfactant character is achieved by the addition of
a small hydrophobic functionality (e.g.,
nonylphenol) to a water-soluble polyethylene oxide
chain. Related materials and methods are disclosed
in U.S. Patent 4,075,411.

Polymerizable surfactants have also been used
to modify the surface properties of solids. One
class of materials used for this purpose are lipids
(non-polymeric materials) which are rendered
polymerizable by the addition of various
functionalities such as methacrylate groups

[Ringsdorf, H., et al., "Hydrophilic Spacer Groups
in Polymerizable Lipids: Formation of Biomembrane
Models form Bulk Polymerized Lipids," J. Am. Chem.
Soc., Vol. 107, pp. 4134-4141 (1985)] and various
vinyl groups [Ringsdorf, H., et al., "Saturated and
Polymerizable Amphiphiles with Fluorocarbon Chains.
Investigation in Monolayers and Liposomes," J. Am.
Chem. Soc., Vol. 106, pp. 7687-7692 (1984)]. These
polymerizable lipid surfactants have been used to
prepare liposomes used in the formation and
stabilization of biomembrane models (often referred
to as polymeric liposomes).

Polyfunctional polymerizable surfactants have
also been used in coatings to modify the surface
properties of polymeric objects. European Patent
Publication No. 153,133 (hereinafter "Regen").
Preferred polymerizable surfactants taught by Regen
are polyfunctional lipids. Regen teaches that
monofunctional polymerizable surfactants are
ineffective for modifying surfaces of polymeric
objects. Other polyfunctional polymerizable
surfactants are disclosed in U.S. Patent No.
3,541,138.

An object of Regen was to overcome the
limitations of Langmuir-Blodgett processes,
especially when applied to more complex surface
topographies. Polymerizable surfactants have of
course been employed in Langmuir-Blodgett films.
These multilayer surfactant assemblies are exploited
in microlithography and other opto-electronic
systems. Fendler, J.H., "Polymerized Monolayers
from a Styrene Functionalized Surfactant," Colloids
and Surfaces, Vol. 35, pp. 343-351 (1989).

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Contact lenses are conventionally produced by one of three general techniques--lathing, static casting, and spin casting. Combinations are also known. For example, semi-finished buttons (having one final lens surface) may be formed by static or spin casting and the second lens surface may be produced by lathing. Static and spin casting have the advantage of producing lenses with fewer processing steps than lathing. In either of the molding techniques, the anterior and posterior surfaces of the lens may be formed in one step. Static casting does this by providing two mold surfaces; spin casting does this by providing a mold surface to form the anterior surface and by using the forces generated by spinning liquid monomer to form the posterior surface.

One of the challenges faced when producing lenses by molding is achieving release of the lenses from the molds without damaging the lens surfaces. The phenomenon of lens adherence is a consequence of chemical interactions between mold surfaces and monomer mixtures during polymerization. Among the proposals to meet this challenge is U.S. Patent 4,534,916, which teaches adding (nonpolymerizable) surfactants to the monomer mix. The surfactant addition is reported to improve the surface quality of lenses by decreasing the number of surface defects resulting from mold release (especially of xerogel lenses).

The '916 patent seeks improved surface quality by reducing lens damage during demolding. Others have sought to improve surface quality more

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directly--by surface modifications. For example,
U.S. 4,546,123 teaches covalent attachment of
(nonpolymerizable) surfactant molecules to a
hydrogel lens surface.

The macromonomer technique for preparing graft
copolymers of controlled architecture is well known.
Macromonomers or macromers are polymers of molecular
weight ranging from the hundreds to tens of
thousands, with one of the end groups functionalized
to enter into further polymerization. Milkovich,
Chiang and Schultz demonstrated the synthesis and
applications of a variety of macromers.
R. Milkovich, M.T. Chiang, U.S. Patent No. 3,842,050
(1974); Schultz, G.O. and Milkovich, R., J. App.
Polym. Sci., 27, 4773 (1982); Schultz, G. O. &
Milkovich, R., J. Polym. Sci. Polym. Chem. Ed., 22,
1633 (1984).

Yamashita, Y.; "Synthesis and Application of
Fluorine Containing Graftcopolymers," Polymer Bull.,
5, 335-340 (1981); "Synthesis and Characterization
of Functional Graft Copolymers by Macromonomer
Technique", J. Appl. Polym. Sci., 36, 193-199
(1981); "Synthesis of N-Hydroxyethyl-N-
Methylmethacrylamide and Its Use in the Macromonomer
Synthesis", J. Polym. Sci., Polym. Letters Ed., 19,
629-636 (1981); (hereinafter "Yamashita") teaches a
method of making macromers and the use of macromers
to make graft copolymers. Yamashita used free
radical polymerization in the presence of an
effective chain transfer agent which controlled the
molecular weight of the final macromer and also
provided a functional end group. Thioglycolic acid,
for example, is an effective chain transfer agent

which provides a carboxylic acid functional end
group. The end group can subsequently be reacted
with, e.g., glycidyl methacrylate to give a terminal
methacrylate polymerizable group. Yamashita used
macromers of MMA to prepare graft copolymers of
fluoroalkyl acrylates with polyMMA grafts.
Yamashita does not teach the synthesis of
polymerizable surfactants by the macromonomer
technique.

SUMMARY OF THE INVENTION

A new class of polymerizable surfactants has
now been found that modify the surface properties of
a polymeric object. The polymerizable surfactants
are novel surface active macromonomers described by
the formula:

$$DC[A_xB_y]$$

wherein A is at least one ethylenically unsaturated
hydrophilic monomer, B is at least one ethylenically
unsaturated hydrophobic monomer, C is a functional
chain transfer agent, D is an ethylenically
unsaturated end group, y is within the range from
about 0.1 to about 0.9, and x + y = 1. In a
preferred embodiment, the polymeric object is a
contact lens.

A further aspect of this invention is a novel
class of random copolymers prepared by
copolymerizing at least one ethylenically
unsaturated hydrophobic monomer and at least one
ethylenically unsaturated hydrophilic monomer in the
presence of a functional chain transfer agent.

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Preferred copolymers may be described by the formula:

$$C[A_x B_y]$$

wherein A is at least one ethylenically unsaturated hydrophilic monomer, B is at least one ethylenically unsaturated hydrophobic monomer, C is a functional chain transfer agent, y is within the range of about 0.1 to about 0.9, and x + y = 1. These random copolymers may be used to prepare the novel surface active macromonomers of this invention by adding an ethylenically unsaturated end group to the novel random copolymers.

DETAILED DESCRIPTION OF THE INVENTION

Notations such as "(meth)acrylate" or "(meth)acrylamide" are used herein to denote optional methyl substitution. Thus, methyl (meth)acrylate includes both methyl acrylate and methyl methacrylate and N-alkyl (meth)acrylamide includes both N-alkyl acrylamide and N-alkyl methacrylamide.

The novel random copolymers of this invention can be prepared by copolymerizing at least one ethylenically unsaturated hydrophobic monomer and at least one ethylenically unsaturated hydrophilic monomer in the presence of a functional chain transfer agent. Preferred copolymers may be described by the formula:

$$C[A_x B_y]$$

wherein A is at least one ethylenically unsaturated hydrophilic monomer, B is at least one ethylenically unsaturated hydrophobic monomer, C is a functional

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chain transfer agent, y is within the range of about
0.1 to about 0.9, and x + y = 1.

Suitable ethylenically unsaturated hydrophilic
monomers ("A" in the above formula) include
ethylenically unsaturated polyoxyalkylenes,
polyacrylamides, polyvinylpyrrolidones, polyvinyl
alcohols, poly (hydroxyethyl methacrylate) or poly
(HEMA), and N-alkyl-N-vinyl acetamides. Ethylenic
unsaturation may be provided by (meth)acrylate,
(meth)acrylamide, styrenyl, alkenyl, vinyl carbonate
and vinyl carbamate groups. Preferred hydrophilic
macromonomers include methoxypolyoxyethylene
methacrylates of molecular weights from 200 to
10,000, more preferred are methoxypolyoxyethylene
methacrylates of molecular weight range of 200 to
5,000 and most preferred are methoxypolyoxyethylene
methacrylates of molecular weight range of 400 to
5,000. Additional preferred hydrophilic
macromonomers include poly-N-vinylpyrrolidone
methacrylates of molecular weights of 500 to 10,000.
More preferred are poly-N-vinylpyrrolidone
methacrylates of molecular weights of 500 to 5,000
and most preferred are poly-N-vinylpyrrolidone
methacrylates of molecular weights of 1000 to 5,000.
Other preferred hydrophilic macromonomers include
poly-N,N-dimethyl acrylamide methacrylates of
molecular weights of 500 to 10,000. More preferred
are poly-N,N-dimethyl acrylamide methacrylates of
molecular weights of 500 to 5,000 and most preferred
are poly-N,N-dimethyl acrylamide methacrylates of
molecular weights of 1000 to 5,000.

Suitable ethylenically unsaturated hydrophobic
monomers ("B" in the above formula) include alkyl

(meth)acrylates, N-alkyl (meth)acrylamides, alkyl
vinylcarbonates, alkyl vinylcarbamates, fluoroalkyl
(meth)acrylates, N-fluoroalkyl (meth)acrylamides, N-
fluoroalkyl vinylcarbonates, N-fluoroalkyl
vinylcarbamates, silicone-containing
(meth)acrylates, (meth)acrylamides, vinyl
carbonates, vinyl carbamates, styrenic monomers
[selected from the group consisting of styrene,
alpha-methyl styrene, para-methyl styrene, para-t-
butyl monochloro styrene, and para-t-butyl dichloro
styrene] and polyoxypropylene (meth)acrylates.
Preferred hydrophobic monomers include methyl
methacrylate, dodecyl methacrylate, octafluoropentyl
methacrylate, perfluorooctyl methacrylate,
methacryoyl oxypropyl tris(trimethylsiloxy)silane
(TRIS).

The functional chain transfer agent ("C" in the
above formula) controls the molecular weight of the
copolymer and provides appropriate functionality for
subsequent addition of a polymerizable group.
Suitable functional chain transfer agents include
mercapto carboxylic acids, mercapto alcohols (also
known as hydroxymercaptans), and aminomercaptans.
Preferred chain transfer agents include thioglycolic
acid, 2-mercaptoethanol and 2-aminoethane thiol.
The molar ratio of chain transfer agent to total
monomer content used in the copolymerization is
preferably in the range of 0.01 to 3, more
preferably in the range of 0.02 to 2, and still more
preferably in the range of 0.05 to 1.

The novel surface active macromonomers of this
invention are described by the formula:

$$DC[A_x B_y]$$

wherein A, B, C, x and y are as described above and
D is an ethylenically unsaturated end group.

Selection of the ethylenically unsaturated end
group ("D" in the above formula) is determined by
the functional group of the functional chain
transfer agent. For example, if the chain transfer
agent contains a carboxylic acid group, glycidyl
methacrylate can provide a methacrylate end group.
If the chain transfer agent contains hydroxy or
amino functionality, isocyanato ethyl methacrylate
or (meth)acryloyl chloride can provide a
methacrylate end group and vinyl chloro formate can
provide a vinyl end group. A wide variety of
suitable combinations of ethylenically unsaturated
end groups and functional chain transfer agents will
be apparent to those skilled in the art. The
foregoing is intended to be illustrative, not
limiting.

Varying the ratio of hydrophilic monomer to
hydrophobic monomer changes the surface properties
of polymeric objects made from the surface active
macromers. For example, when preparing contact
lenses containing certain surface active macromers
of this invention, it has been found that higher
amounts of hydrophilic component optimized mold
release characteristics of the lenses but that
optimum clinical performance was obtained with a
relatively lower amount of hydrophilic component.
Accordingly, the selection of a particular ratio
will be governed by the particular surface
properties ultimately sought for the polymeric
object. Generally, however, y is preferably in the
range from about 0.1 to about 0.9, more preferably

in the range from about 0.3 to about 0.9, and still
more preferably in the range from about 0.5 to about
0.8.

The random copolymers of this invention are
formed by a free radical mechanism using a wide
variety of known free radical catalysts such as the
diacyl peroxides (e.g., benzoyl peroxide); dialkyl
peroxides (e.g., di-tert-butyl peroxides); ketone
peroxides (e.g., methylethyl ketone peroxide); and
peresters which readily hydrolyze (e.g., tert-butyl
peracetate, tert-butyl perbenzoate, di-tert-butyl
diperphthalate). A particularly useful class of
peroxy initiators are the organic hydroperoxides
such as cumene hydroperoxide, methylethyl ketone
hydroperoxide, tert-butyl hydroperoxide, etc. The
initiators should be used at a concentration of
about 0.01 to about 10 % by weight of the total
formulation, preferably about 0.1 to about 5 %.
Another class of initiators comprises carbonyl-
containing ultraviolet-activated free radical
generators, such as acetophenone, benzophenone, and
benzoin ethers. Other suitable UV initiators and
initiator mixtures will be apparent to one of
ordinary skill in the art.

Solvents can be used in the process. Solvent
choice will depend upon the solubility parameters of
the comonomers used and should be chosen to allow
full solubilization of all polymerizate components.
Preferred solvents include tetrahydrofuran, dioxane,
chloroform, dichloromethane, methanol and mixtures
of these solvents.

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The surface-active macromers of this invention
may be used to modify the surfaces of polymeric
objects in two ways. In the first, the surface-
active macromer is added to the monomer mix used to
form the polymeric object. In the second, the
polymeric object is immersed in an aqueous
dispersion of the surface-active macromer, a cross-
linking agent, and a free radical initiator and the
immersion is exposed to ultraviolet light to form a
permanent, cross-linked surface coating on the
object. Illustrations of these techniques are shown
in the Examples of this application.

The polymeric objects whose surfaces may be
modified by these techniques include polymers having
a wide variety of compositions and shapes.
Polymeric objects of particular concern in the
development of this invention were contact lenses
and the particular surface modification sought was
to increase surface wettability without sacrificing
otherwise beneficial bulk properties of the
polymeric material (especially oxygen permeability).
Although the utility of the macromonomers of this
invention will be further illustrated by referring
particularly to their incorporation into contact
lenses, it will be understood that the utility of
the macromonomers of this invention is not so
limited.

One class of contact lenses whose surface may
be usefully modified by the macromonomers of this
invention are soft hydrogel lenses. Conventional
monomer systems for such lenses employ a hydrophilic
monoolefinic monomer (i.e., a monoethylenically
unsaturated monomer) and a polyolefinic (usually

diolefinic) monomer (e.g., a polyethylenically
unsaturated compound which functions as a cross-
linking agent) in an amount sufficient to
insolubilize the resulting hydrophilic hydrogel but
insufficient to destroy the hydrophilic properties.
Mixtures of hydrophilic monoolefinic monomers are
used as well as mixtures of cross-linking agents.
Other monomers which are copolymerizable with the
hydrophilic monomer are also used to adjust various
properties of the polymeric material, as is well
known in the art.

Illustrative hydrophilic monomers include water
soluble monoesters of (meth)acrylic acid with an
alcohol having an esterifiable hydroxyl group and at
least one additional hydroxyl group such as the
mono- and poly-alkylene glycol monoesters of
(meth)acrylic acid, e.g., ethylene glycol
mono(meth)acrylate, diethylene glycol
mono(meth)acrylate, propylene glycol
mono(meth)acrylate, dipropylene glycol
mono(meth)acrylate, and the like; the N-alkyl and
N,N-dialkyl substituted (meth)acrylamides such as N-
methyl (meth)acrylamide, N,N-dimethyl
(meth)acrylamide, and the like; N-vinylpyrrolidone
and the alkyl substituted N-vinyl pyrrolidones;
glycidyl (meth)acrylates; the unsaturated amines;
the alkoxy ethyl acrylates; mixtures thereof; and
others known to the art.

Illustrative di- or higher polyfunctional
species employed as cross-linking agents are
divinylbenzene, ethylene glycol di(meth)acrylate,
propylene glycol di(meth)acrylate, and the
(meth)acrylate esters of polyols such as

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triethanolamine, glycerol, pentaerythritol, butylene
glycol, diethylene glycol, triethylene glycol,
tetraethylene glycol, mannitol, and sorbitol.
Further illustrations include N,N-methylene-bis-
(meth)acrylamide, sulfonated divinylbenzene, and
divinylsulfone.

Illustrative of other copolymerizable monomers
are hydrophobic (meth)acrylic esters such as alkyl
(meth)acrylates wherein the alkyl moiety contains 1-
5 carbon atoms.

While soft, hydrophilic, gel-type lenses may be
modified by the macromonomers of this invention, of
greater interest is the modification of lenses
prepared from a formulation including at least one
silicone monomer and at least one hydrophilic
monomer. Included in this class of materials are
soft contact lens formulations (both hydrogel and
nonhydrogel) and rigid gas permeable contact lens
formulations.

Preferred soft hydrogel formulations are those
described in U.S. Patent Application Serial Nos.
07/363,662 filed June 7, 1989 and 07/364,204 filed
May 2, 1989, the entire contents of which are
incorporated herein by reference. Other examples of
useable formulations are found in U.S. Patent
Nos. 4,136,250; 4,740,533; 4,711,943; 4,189,546; and
4,153,641.

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One type of presently preferred hydrogel
formulations incorporate urethane prepolymers of the
general formula:

$$E(*D*A*D*G)_a*D*A*D*E' \text{ or}$$

$$E(*D*G*D*A)_a*D*G*D*E'$$
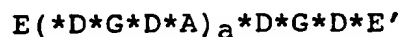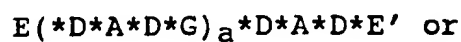
where

A denotes a divalent polymeric radical
represented by the general formula chosen from the
group of

$$- (CH_2)_{1-4} \left(\begin{array}{c} R^S \\ | \\ Si-O \\ | \\ R^S \end{array} \right)_p \begin{array}{c} R^S \\ | \\ Si \\ | \\ R^S \end{array} -(CH_2)_{1-4} --$$
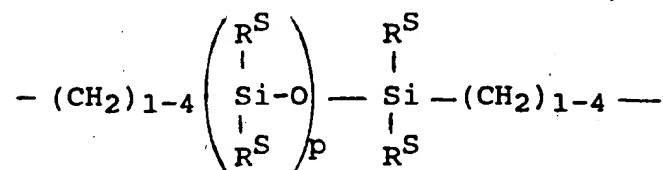
wherein R^S denotes an alkyl radical or a short chain

fluorinated alkyl radical with 1 to

3 carbon atoms; and

p provides a moiety weight of 400 to 10,000;

D denotes an alkyl diradical, an alkyl

cycloalkyl diradical, a cycloalkyl

diradical, an alkylaryl diradical or an

aryl diradical, with 6 to 30 carbon atoms;

G denotes an alkyl diradical, a cycloalkyl

diradical, an alkyl cycloalkyl diradical,

an aromatic diradical or an alkylaromatic

diradical with 1 to 40 carbon atoms which

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may have ether, thio, or amine linkages in
the main chain;

* denotes a urethane or ureido linkage; and

E and E' denote polymerizable unsaturated

organic radicals represented by the

general chemical formula

$$R^3CH=\overset{\overset{\textstyle R^2}{\textstyle |}}{C}\ (CH_2)_w\ (X)_x\ (Z)_z\ (Ar)_y-R^1-$$
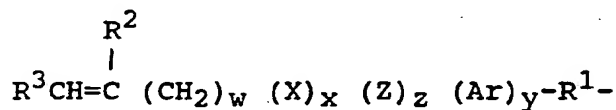
wherein R^1 denotes a divalent alkylene radical with

1 to 10 carbon atoms;

R^2 denotes a -H or $-CH_3$ radical;

R^3 denotes a -H radical or an alkyl radical

with 1 to

6 carbon atoms or a $-\overset{\overset{\textstyle O}{\textstyle ||}}{C}Y-R^4$ radical where

Y is -O-, -S- or -NH- and R^4 denotes

an alkyl radical with 1 to

12 carbon atoms;

X denotes $-\overset{\overset{\textstyle O}{\textstyle ||}}{C}-$, or $-O-\overset{\overset{\textstyle O}{\textstyle ||}}{C}-$;

Z denotes -O-, -S-, or -NH-;

Ar denotes an aromatic radical with 6 to

30 carbon atoms;

a is at least 1;

w is 0 to 6;

x is 0 or 1;

y is 0 or 1; and

z is 0 or 1.

The isocyanates which can be used in preparation
of these urethane prepolymers include toluene
diisocyanate, 4,4'-diphenyl diisocyanate, 4,4'-
diphenylene methane diisocyanate, p-phenylene
diisocyanate, dianisidine diisocyanate, 1,5
napthalene diisocyanate, 4,4'-diphenyl ether
diisocyanate, 4,4'(dicyclohexyl)methane
diisocyanate, 1,3-bis-(isocyanato
methyl)cyclohexane, cyclohexane diisocyanato,
tetrachlorophenylene diisocyanate, isophorone
diisocyanate, and 3,5-diethyl-4,4'-diisocyanato
diphenyl methane.

Other diisocyanates which may be used are higher
molecular weight diisocyanates formed by reacting
polyamines which are terminally capped with primary
or secondary amines, or polyhydric alcohols with
excess of any of the above described diisocyanates.
In general, these high molecular weight
diisocyanates will have the general formula

$$[O=C=N-R-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\parallel}}{C}-X]_2-B$$
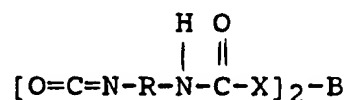
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wherein R is a divalent organic radical with 2 to
about 20 carbon atoms, X is -O-, or -NR'-, where R
is -H or a lower alkyl, and B is a divalent organic
radical.

The diisocyanate is reacted with low molecular
weight diols or glycols such as 2,2-(4,4'
dihydroxydiphenyl)-propane (bisphenol-A); 4,4'-iso-
propylidine dicyclohexanol (hydrogenated biphenol-
A); ethoxylated bisphenol-A; propoxylated bisphenol-
A; 2,2-(4,4'-dihydroxydiphenyl)-pentane; α,α'-(4,4'-
dihydroxydiphenyl)-p-diisopropyl benzene; 1,3
cyclohexane diol; 1,4-cyclohexane diol; 1,4-
cyclohexane dimethanol; bicyclic and tricyclic diols
such as 4,8-bis-(hydroxymethyl)-tricyclo
$[5.2.1.0^{2,6}]$ decane, neopentyl glycol, 1,4
butanediol, 1,3-propanediol, 1,5-pentanediol,
diethylene glycol, triethylene glycol and the like.

These hard segments form hard domains in the
final polymer or copolymer by association via
hydrogen bonding with other rigid segments. The
degree of association within the hard domain can be
modified by controlling the amount of hydrogen
bonding between the segments by either 1) decreasing

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the overall weight content of the hard segment in
the prepolymer by increasing the molecular weight of
the soft segment or 2) by decreasing the amount of
hydrogen bonding density in the hard segment by
either using relatively soft, longer chained diols,
or by using primary amines or secondary amines
capped low molecular weight compounds in conjunction
with the diisocyanates rather than the diols.

The hard segments are then reacted with a
relatively high molecular weight polymer which is
$\alpha,\omega-$ endcapped with two active hydrogens, usually
hydroxyl groups. These segments form the so-called
soft segment of the prepolymer. Various types of
high molecular weight polymers can be used including
in general polymers of the following formulae

a) $HO\ (CH_2)\ (R^PO)_n\ (CH_2)\ OH;$

b) $HO\ (CH_2)\ (R^PO)_m\ (CH_2)\ OH;$ and

c) $HO\ (CH_2)_{1-4} \left[\begin{array}{c} R^S \\ | \\ Si-O \\ | \\ R^S \end{array} \right]_m \begin{array}{c} R^S \\ | \\ Si - (CH_2)_{1-4}\ OH \\ | \\ R^S \end{array}$
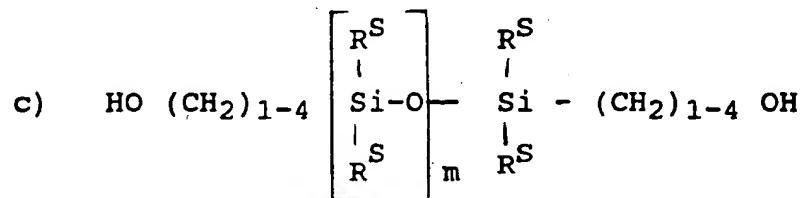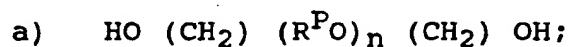
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Formulae a) represents polyoxyalkyleneglycols.

These diols include polymers prepared from the

epoxides: ethylene oxide 1,2-propylene oxide, 1,2-

butylene oxide, 2,2 epoxydecane, 1,2-epoxyoctane,

2,3-epoxy norborane, 1,2-epoxy-3-ethoxy propane,

2,2-epoxy-3-phenoxypropane, 2,3-epoxypropyl-4-

methoxy phenyl ether, tetrahydrofluran, 1,2-epoxy-3-

cyclohexyloxy propane, oxetane, 1,2-epoxy-5-hexene,

1,2-epoxyethylbenzene, 1,2-epoxy-1-methoxy-2-

methylpropane, benzyloxy propylene oxide, the like

and combinations thereof.

The preferred polymers of this class are

polypropylene glycols of molecular weights, 2000,

3000 and 4000 and more and polyoxyethylene

polyoxypropylene block copolymers with molecular

weight greater than 2000.

Formulae b) represents polyfluoroethers with

α,ω- active hydrogens. This class of polymers can

be synthesized as taught in U.S. Patent No.

3,810,874. Generally, these polymers should have

molecular weights between 400 and 10,000.

Formulae c) represents α,ω- dihydroxyl alkyl

endblocked polysiloxane which for the purpose of the

present invention should have a molecular weight in
the range of 400 to 10,000. These polysiloxanes can
be synthesized by reacting a disiloxane of the
general formula

$$HO \ (CH_2)_{1-4} \ \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}} \ (CH_2)_{1-4} \ OH$$
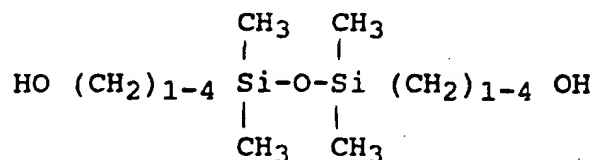
with cyclopolydimethyl siloxane under acidic
conditions.

    Alternately, the disiloxane can be replaced with
dimethoxydimethylsilane or diethoxy dimethyl silane
to produce the $\alpha,\omega-$ dihydroxy endcapped
polysiloxanes.

    The endcapping monomers used in the prepolymer
are generally represented by the formula

$$R^3CH=\overset{\overset{\displaystyle R^2}{|}}{C} \ (CH_2)_w \ (X)_x \ (Z)_z \ (Ar)_y \ -R^1-$$
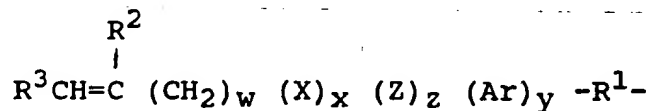
as defined supra. The Stage B reaction product is
reacted with an excess of suitable acrylate or
methacrylate esters containing a hydroxy or amine

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group on the non-acrylate or non-methacrylate

portion of the monomer to form the endcaps of the

above formula. Suitable endcap monomers include

hydroxyethyl acrylate, hydroxyethyl methacrylate,

aminoethyl methacrylate, 3 hydroxypropyl

methacrylate, amino propyl methacrylate,

hydroxyhexylacrylate, t-butylaminoethyl

methacrylate, monoacrylate or monomethacrylate

esters of bisphenol-A and/or bisphenol-B.

The urethane prepolymers are formed by two

general synthetic approaches. One approach produces

the hard-soft-hard prepolymer while the second

approach produces the soft-hard-soft prepolymer.

The scheme used to produce hard-soft-hard

urethane prepolymer employed three stages. In the

first stage (STAGE A) 2 mole equivalents of

diisocyanate are reacted with about 1 mole

equivalent low molecular weight diols. If these

diols are represented by the symbol ◆G◆, where ◆

denotes a hydroxyl radical and G represents the rest

of the diol compound, and the diisocyanate

functional compound is represented by •D• where •

represents an isocyanate radical, the STAGE A

reaction can be schematically represented as follows:

$$2 \bullet D \bullet \ + \ \bullet G \bullet \ \longrightarrow \ \bullet D*G*D \bullet$$

where * denotes a urethane or a ureido linkage. STAGE A produces a so-called "Hard" segment. As is known to those skilled in polymer chemistry, the product $\bullet D*G*D \bullet$ is the mathematical average of all reaction product molecules. The reaction product of the actual reaction will contain $\bullet O \bullet$ and $\bullet D(*G*D)_c *G*D$ with $c \geq 2$. Again, the formulas are numerical averages.

STAGE B involves reacting about one half mole equivalent of a $\alpha, \omega -$ diol endcapped long chain polymer with the reaction product of STAGE A. If $\bullet A \bullet$ represents the long chain diol the STAGE B Reaction is

$$2 \bullet D*G*D \bullet \ + \ \bullet A \bullet \ \longrightarrow \ [\bullet D*G*D*]_2 \bar{A}$$
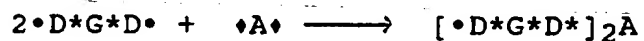
In STAGE C, the reaction product from STAGE B is reacted with a molar excess of an endcapping monomer which has: 1) hydroxyl or amine functionality; and 2) some polymerizable unsaturation. If the

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endcapper is represented by the symbol E♦, where ♦
is -OH or -NH$_2$ or -NH-, the reaction proceeds
generally as

$$[\bullet D*G*D*]_2A + 2E\diamond \longrightarrow [E*D*G*D*]_2A$$
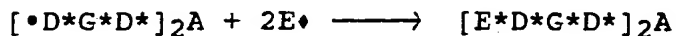
Optionally, STAGE B can be run with molar excess
of ♦A♦ to produce multiblock polymers of the general
formula •(D*G*D*A)$_a$*D*G*D• where a is at least 1.
This reaction product would be endcapped in STAGE C
above.

The second general synthetic scheme using the
same nomenclature described is represented by the
following general formulae:

STAGE A

$$2 \bullet D \bullet + \diamond A\diamond \longrightarrow [\bullet D*]_2A$$

STAGE B

$$2[\bullet D*]_2A + \diamond G\diamond \longrightarrow [\bullet D*A*D*]_2G$$

STAGE C

$$[\cdot D * A * D *]_2 G \ + \ 2E \quad \longrightarrow \quad [E * D * A * D *]_2 G$$

In general, each of the reaction stages is run until the reactive step is complete. Reaction progress in STAGES A and B reactants can be monitored by acid base titration. The isocyanate content was calculated by the difference of acid equivalents between a stock solution dibutylamine and its reaction product with the diisocyanate reaction intermediate. The reaction was also monitored by ATR-IR for the appearance/disappearance of peaks at 1700 cm^{-1}, which indicated the presence of

$$\overset{\text{O}}{\underset{\|}{\text{}}}$$

-C-, and 2250 cm^{-1} which indicated consumption of -N=C=O.

The synthesis of the prepolymer may be run neat or in solution. A wide range of aprotic solvents can be used to synthesize the prepolymers of the present invention. Solvents useful in the synthesis include toluene, methylene, chloride, benzene, cyclohexane, hexane, heptane and the like. Preferred solvents are toluene, methylene chloride and mixtures thereof.

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Reaction of the prepolymer precursors may be accomplished in the presence or absence of catalysts for urethane reactions, such catalysts being well known in the art. The first step of prepolymer synthesis where diisocyanate is first reacted with a short carbon chain (2 to 30 carbon atoms) diol, particularly where an aromatic diisocyanate is used, proceeds very rapidly, even in the absence of any catalyst. In fact, during the step of reacting diisocyanate and short chain diol, temperature control may be required in order to avoid/minimize side reactions.

Preferably, the first step of prepolymer synthesis in accordance with the present invention is carried out below about 100°C, most suitably within the range of from about 60°C to about 90°C. Thereafter, the second step of the reaction is carried out at comparable temperatures, preferably within the range of from about 40°C to 70°C. The final step of prepolymer formation suitably is effected at temperatures of from about room temperature to about 100°C, with a narrow range of from about 40°C to about 50°C being most preferred. As will be apparent to those skilled in the art,

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optimal reaction conditions, such as temperatures
and duration, are selected for each individual
reaction system to achieve conditions that produce a
favorable rate of reaction without fostering
undesirable side reactions.

Among the suitable catalysts for use in
prepolymer formation are tin salts and organic tin
esters, such as dibutyl tin dilaurate, tertiary
amines, such as triethyl diamine and other
recognized catalysts, such as 1,4-diaza (2.2.2)-
bicyclooctane (DABCO).

These silicone-containing urethane prepolymers
may be copolymerized with a wide variety of
hydrophilic monomers to produce soft hydrogel
contact lenses. Hydrophilic monomers suitable for
this use include 2-hydroxyethylmethacrylate, N-vinyl
pyrrolidone, (meth)acrylamide, vinyl acetamide, and
other ethylenically unsaturated hydrophilic
monomers. Further comonomers may also be added to
enhance wetting or to modify other properties as is
generally known to those skilled in the art.

Another presently preferred hydrogel
formulation incorporates silicone-containing vinyl

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carbonate or vinyl carbamate prepolymers of the

general formula:

$$\left[\begin{array}{c} R^2 \qquad\qquad O \\ | \qquad\qquad\quad \| \\ CH_2=C-(CH_2)_b-O-C-X \end{array}\right]_a R^{Si}$$
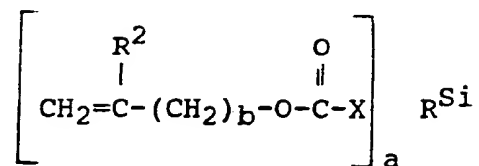
wherein X denotes an -O-, -S-, or -NR^3-

divalent radical;

R^{Si} denotes a silicone containing organic

radical;

R^2 denotes -H or -CH$_3$;

A is 1, 2, 3, or 4; and

b is 0 or 1.

Suitable silicone-containing organic radicals

(R^{Si}) include the following:

$$-(CH_2)n \ Si\left[(CH_2)_m CH_3\right]_3;$$
$$-(CH_2)n \ Si(OSi\left[(CH_2)_m CH_3\right]_3)_3;$$

$$-(CH_2)n \left[\begin{array}{c} R^1 \\ | \\ Si-O \\ | \\ R^1 \end{array}\right]_d R^{Cl}; \ and$$

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$$-(CH_2)_n \begin{bmatrix} R^1 \\ | \\ Si-O \\ | \\ R^1 \end{bmatrix}_d \begin{matrix} R^1 \\ | \\ Si- R^{cl} \\ | \\ R^1 \end{matrix}$$
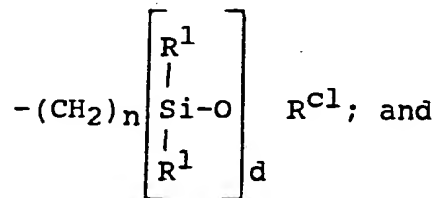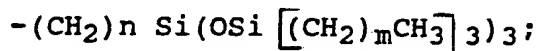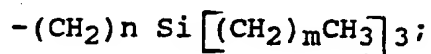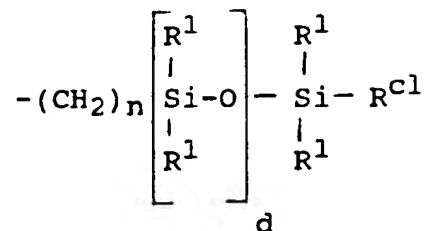
where R^1 denotes a monovalent organic radical such
an an alkyl radical with 1 to 6 carbon atoms, or a
fluoroalkyl radical with 1 to 6 carbon atoms;

R^{cl} denotes

$-(CH_2)_p-O-C-CH=CH_2$
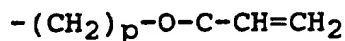
p is 1 to 6; and

d is 1-200, and

where n is 1, 2, 3, or 4, and m is 0, 1, 2, 3, 4, or

5.

The silicone-containing vinyl
carbonate/carbamate monomers specifically include
3-[tris(trimethylsiloxy)silyl]propyl vinyl
carbonate;
1,3-bis[4-(vinyloxycarbonyloxy)but-1-yl]tetramethyl-
disiloxane; 3-(trimethylsilyl)propyl vinyl
carbonate; t-butyldimethylsiloxyethyl vinyl
carbonate; trimethyl-silylmethyl vinyl carbonate;
trimethylsilylethyl vinyl carbonate;
2,2,2-trifluoroethyl vinyl carbonate; t-butyl vinyl
carbonate; 3-[tris(trimethylsiloxy)silyl] propyl

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vinyl carbonate; 2,2,2-trifluoroethyl vinyl
carbamate; 1,1,1,3,3,3-hexafluoro-2-propyl vinyl
carbonate;
3-(vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy
)silane]; 3-[tris-(trimethylsiloxy)silyl]propyl
vinyl carbamate; "V_2D_{25}",
2,2,2-trifluoro-1-phenylethyl vinyl carbonate;
1-adamantane vinyl carbonate, 1-adamantanethyl vinyl
carbonate, 1-adamantaneethyl vinyl carbonate; and
1-adamantane vinyl carbamate.

     Preferred nonhydrogel soft contact lens
formulations are mixtures of polymerizable
polysiloxanes containing fluorinated side chains and
internal wetting agents. Further components such as
toughening agents, crosslinking agents, and other
auxiliary modifiers are desirably present as taught
in U.S. Patent 4,810,764, the entire content of
which is incorporated herein by reference.

     Polymerizable, fluorinated polysiloxanes
employed in this embodiment of the invention are
described by the general formula:

$$A(CH_2)_4 - \begin{bmatrix} R^1 \\ | \\ Si - O \\ | \\ R^2 \end{bmatrix}_m - \begin{bmatrix} R^3 \\ | \\ Si - O \\ | \\ R^4 \end{bmatrix}_n - \begin{matrix} R^1 \\ | \\ Si - (CH_2)_4 - A \\ | \\ R^2 \end{matrix}$$
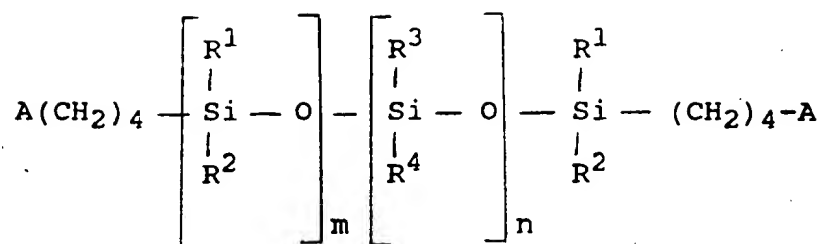
where A denotes an activated unsaturated group, $-R^1$ and R^2 independently denote alkyl radicals with 1 to 6 carbon atoms or phenyl radicals; R^3 and R^4 independently denote alkyl radicals with 1 to 6 carbon atoms, phenyl radicals, or fluorinated alkyl radicals with 1 to 6 carbon atoms, provided that at least one of R^3 or R^4 is a fluorinated alkyl radical with 1 to 6 carbon atoms; m + n is at least 1; and n is at least 1.

Internal wetting agents ("hydrophilic monomers") useful in this embodiment of the invention include N-alkyenoyl trialkylsilyl aminates (hereinafter "NATA") (described in U.S. Patent No. 4,652,622) represented by the general formula

$$CH_2=C(E)C(O)N(H)CH(G)(CH_2)_mC(O)OSi(R)_3$$
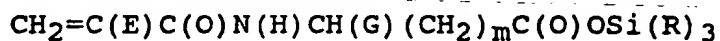
wherein

E is H or CH_3,

G is $(CH_2)_xC(O)OSi(R)_3$ or H,

R is CH_3, C_2H_5 or C_3H_7,

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m is an integer from 1 to 15,

x is an integer from 1 to 10, and

m + x is an integer from 1 to 15

Acryloyl- and methacryloyl-, mono- and dicarboxylic amino acids, hereinafter NAA, impart desirable surface wetting characteristics to polysiloxane polymers, but precipitate out of siloxane monomer mixtures before polymerization is completed. NAA can be modified to form trialkylsilyl esters which are more readily incorporated into polysilocane polymers. The preferred NATA's are trimethylsilyl-N-methacryloylglutamate, triethylsilyl-N-methacryloylglutamate, trimethyl-N-methacryloyl-6-aminohexanoate, trimethylsilyl-N-methacryloyl-aminododecanoate, and bis-trimethylsilyl-N-methacryloyl aspartate.

The preferred internal wetting agents are oxazolones of the general formula
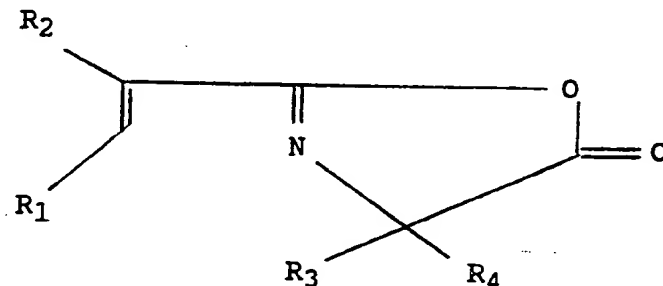
where

R_1 and R_2 independently denote H or CH_3; and

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R$_3$ and R$_4$ independently denote methyl or cyclohexylradicals.

These preferred internal wetting agents specifically include 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one (IPDMO), 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (VDMO), cyclohexane spiro-4'-(2'isopropenyl-2'-oxazol-5'-one) (IPCO), cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) (VCO), and 2-(-1-propenyl)-4,4-dimethyl-oxazol-5-one (PDMO).

These preferred internal wetting agents have two important features which make them particularly desirable wetting agents: (1) They are relatively non-polar and are compatible with the hydrophobic monomers (the polysiloxanes and the toughening agents), and (2) They are converted to highly polar amino acids on mild hydrolysis, which impart substantial wetting characteristics. When polymerized in the presence of the other components, a copolymer is formed. These internal wetting agents result through the carbon-carbon double bond with the endcaps of the polysiloxane monomers, and with the toughening agents to form copolymeric

materials particularly useful in biomedical devices,
especially contact lenses.

These oxazolones are prepared by the general
reaction sequence

$$
\underset{\substack{R_2 \\ R_1}}{\overset{O}{\underset{}{\big\|}}}\!\!\!-Cl \;+\; H_2N-\underset{\substack{| \\ COOH}}{\overset{R_3}{\overset{|}{C}}}-R_4 \qquad \xrightarrow[\substack{H_2O \\ 0°C.}]{NaOH}
$$

(I)   (II)

$$
\underset{\substack{R_2 \\ R_1}}{\overset{O}{\underset{}{\big\|}}}\!\!\!-NH-\underset{\substack{| \\ COOH}}{\overset{R_3}{\overset{|}{C}}}-R_4 \qquad \xrightarrow[\text{Hexane}]{\overset{O}{\overset{\|}{ClCOC_2H_5}}}
$$

```
      R2
        \
         \
          \
           _____ O
           ‖
           ‖
    R1 ____/                    ‖
                     N          ‖
                      \         ‖ == O
                       \       /
                        \     /
                      R3      R4
```
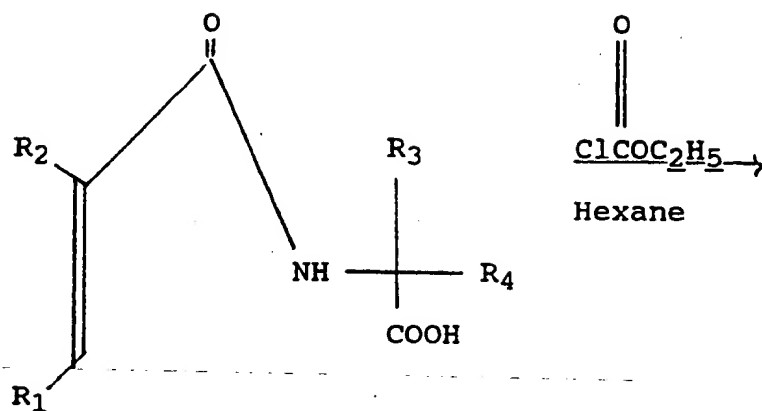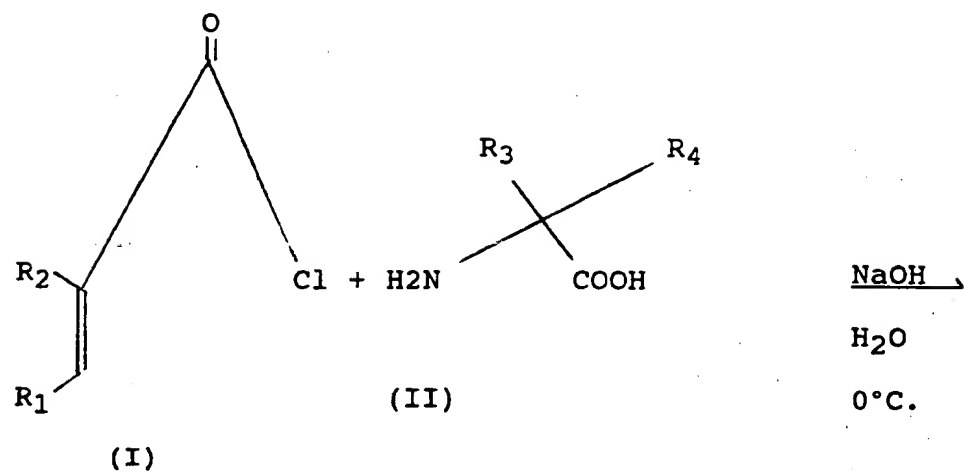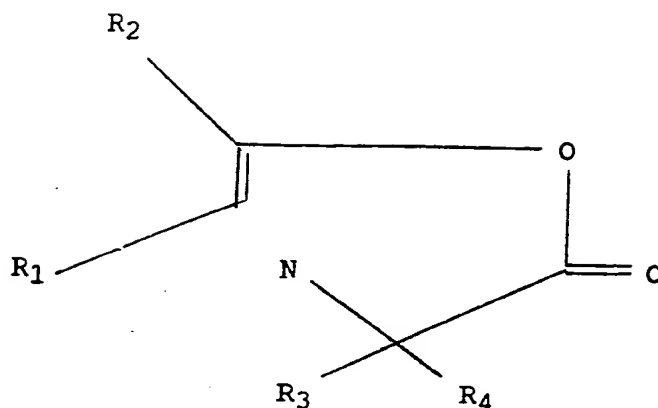
The first step is a Shotten-Bauman acrylation
of an amino acid. Upon completion of this step the
polymerizable functionality is introduced by using
either acryloyl or methacryloyl chloride.

Rigid gas permeable contact lens formulations
which are suitable for the practice of this
invention are silicone-based copolymers prepared
from siloxanylalkyl esters of methacrylic acid and
other acrylate, methacrylate, or itaconate monomers
in many known formulations. See U.S. Patent
Nos. 4,424,328; 4,463,149; 4,664,479; and 4,686,267
for examples of such formulations.

This invention is further described by the
following Examples, which are intended to be
illustrative, not limiting.

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EXAMPLES

SYNTHESES OF RANDOM COPOLYMERS

EXAMPLE 1

Polymerization of 1-Vinyl-2-pyrrolidinone

Distilled 1-vinyl-2-pyrrolidinone, (NVP) 40 g,
2-mercaptoethanol, 2.80 g and azobisisobutyronitrile
(AIBN, recrystallized from ethanol) 0.59 g were
combined with 100 mL of anhydrous tetrahydrofuran
(THF) in a 250 mL three neck flask. The flask was
also fitted with a mechanical stirrer and a reflux
condenser. A slow stream of nitrogen was used to
deoxygenate the solution for 15 minutes. After
24 hours of reflux under a nitrogen atmosphere, no
vinyl protons could be detected in the 60 Mhz NMR
spectra (6.5-7.0 ppm). The hydroxy-terminated
polymer was precipitated from 2 L of anhydrous ethyl
ether. The solid was dissolved in 200 ml of THF and
the precipitation repeated twice. The white solid,
29.37 g (69% yield), was dried under reduced
pressure.

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EXAMPLE 2

Synthesis of a Polyvinyl Pyrrolidinone (PVP)
Macromer

Hydroxy-terminated PVP, 9.0 g (from Example 1),
was dissolved in 90 mL of chloroform, in a 250 mL
3-neck flask fitted with a magnetic stirrer, a
reflux condenser, and an addition funnel.
Dibutyltin dilaurate, 32.5 mg, and butylated hydroxy
toluene, 2.1 mg (BHT), were added. Isocyanatoethyl
methacrylate, 0.86 g (ICEM) in 10 mL $CHCl_3$, was
added dropwise. Following the addition the solution
was heated to reflux. After 3 hours no ICEM could
be detected by infrared analysis. The reaction
mixture was then slowly added to 6 L of anhydrous
ethyl ether and the solid collected. Precipitation
of the PVP macromer was repeated, from ethanol into
4 L of ethyl ether. After drying at 30°C under
reduced pressure the yield of macromer was 7.1 g
(78%). The Mn (number average molecular weight) and
Pd (polydispersity) values were 1,986 and 1.4 (vs.
polyethylene glycol standards).

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EXAMPLE 3

Copolymerization of OFPMA and PVP Macromer

1H,1H,5H Octafluoropentylmethacrylate, (OFPMA)
0.75 g, PVP macromer (Example 2), 5.0 g,
2-mercaptoethanol, 105 uL, and AIBN (recrystallized
from ethanol), 8.2 mg, were combined with 100 mL of
anhydrous tetrahhdrofuran (THF) in a 250 mL three
neck flask. The flask was also fitted with a
mechanical stirrer and a reflux condenser. A slow
stream of nitrogen was used to deoxygenate the
solution for 15 minutes. After 20 hours of reflux
under a nitrogen atmosphere the hydroxy terminated
polymer was precipitated from 2 L of anhydrous ethyl
ether. The solid was dissolved in 200 ml of THF and
the precipitation repeated once. The white solid
was dried under reduced pressure leaving 4.14 g, a
72% yield.

EXAMPLE 4

Polymerization of N,N-Dimethylacrylamide(DMA)

Distilled DMA, 20 g, 2-mercaptoethanol, 280 uL,
and AIBN (recrystallized from ethanol), 0.33 g, were
combined with 100 mL of anhydrous tetrahhyrofuran

(THF) in a 250 mL three neck flask. The flask was
also fitted with a mechanical stirrer and a reflux
condenser. A slow stream of nitrogen was used to
deoxygenate the solution for 15 minutes. After
20 hours of reflux under a nitrogen atmosphere no
vinyl protons could be detected in the 60 Mhz NMR
spectra (6.5-7.0 ppm). The hydroxy terminated
polymer was precipitated from 2 L of anhydrous ethyl
ether. The solid was dissolved in 100 ml of THF and
the precipitation repeated. The white solid was
dried under reduced pressure at 30°C. The yield was
15.5 g and the Mn (number average molecular weight),
Mw (weight average molecular weight) and Pd
(polydispersity) values were 6,700, 11,318 and 1.7
(vs. polyethylene glycol standards).

EXAMPLE 5

Preparation of a DMA Macromonomer

Hydroxy terminated copolymer, 12 g (from
Example 4) was dissolved in 90 mL of chloroform, in
a 250 mL 3-neck flask fitted with a magnetic stirrer
and a reflux condenser and an addition funnel.
Dibutyltin dilaurate, 36.9 mg, and butylated hydroxy
toluene (BHT), 10.2 mg, were added. Isocyanatoethyl

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methacrylate, 0.30 g (ICEM) in 10 mL CHCl$_3$, was
added dropwise. Following the addition the solution
was heated to reflux. After 48 hours no ICEM could
be detected by infrared analysis. The reaction
mixture was then slowly added to 2 L of anhydrous
ethyl ether and the solid collected. The
precipitation was repeated a second time followed by
drying at 30°C under reduced pressure. The yield of
macromer was 8.6 g. The Mn, Mw and Pd values were
4,400, 7,900 and 1.8 (vs. polyethylene glycol
standards).

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EXAMPLE 6

Copolymerization of OFPMA and DMA Macromer

OFPMA, 1.2 g, DMA macromer (Example 5), 6.7 g, 2-mercaptoethanol, 105 uL, and AIBN (recrystallized from ethanol), 8 mg, were combined with 100 mL of anhydrous tetrahhdrofuran (THF) in a 250 mL three-neck flask. The flask was also fitted with a magnetic stirrer and a reflux condenser. A slow stream of nitrogen was used to deoxygenate the solution for 15 minutes. After 72 hours of reflux under a nitrogen atmosphere the conversion to copolymer was 44%, (by NIR analysis). Addition of 25 mg AIBN and 48 hours refluxing, (120 hours total) gave a 60% conversion to copolymer. Precipitation into 2 L of anhydrous ethyl ether, followed by drying at reduced pressure left 6 g of copolymer with Mn, Mw, and Pd values of 4,600, 8,100, and 1.8 (vs. PEG standards).

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EXAMPLES 7-10

Copolymerization of 1H,1H,5H

Octafluoropentylmethacrylate

and Methoxy polyethylene glycol monomethacrylates

Example 7

A solution was prepared by dissolving 9.1 g of
methoxy polyethylene glycol 1,000 monomethacrylate
in 100 mL of toluene. The solution was carefully
transferred to a 250 mL three neck flask fitted with
a magnetic stirrer and a condenser. To this, 9.1 g
of 1H,1H,5H Octafluoropentylmethacrylate (OFPMA),
1.26 g of distilled thioglycolic acid (TGA) and
0.071 g of azobisisobutyronitrile (AIBN) were added.
AIBN was recrystallized from ethanol before use.
The solution was then deoxygenated using nitrogen
for 15 minutes and then placed under a passive
nitrogen blanket. After stirring for 16 hours at
60°C the percent conversion was determined to be 95-
98% by near infrared (NIR) analysis. The number
average molecular weight was determined by size
exclusion chromatography ("SEC") vs. polystyrene and
by end group titration. The Mn values were 2,902
and 1,815 respectively. Results are shown in
Table I.

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Examples 8-9

The procedure of Example 7 was repeated using higher relative amounts of methoxy polyethylene glycol 1000 monomethacrylate.   THF replaced toluene as the solvent in Example 9.   Results are shown in Table I.

Example 10

The procedure of Example 7 was repeated using methoxy polyethylene glycol 5000 monomethacrylate and using THF as the solvent.   Results are shown in Table I.

Table I

ACID TERMINATED COPOLYMERS

Example #	Type	Composition	Solvent	Rxn time	Mn	Mw	Pd
7	OFPMA/Peo 1k	80/20	Toluene	16h	2902	5370	1.8
8	OFPMA/Peo 1k	70/30	Toluene	72h	2300	3400	1.44
9	OFPMA/Peo 1k	50/50	THF	24h	3163	5287	1.7
10	OFPMA/Peo 5k	80/20	THF	24h	12.6k	9400	1.34

EXAMPLE 11

Copolymerization of

3-Methacryloyloxypropyltris(trimethylsiloxy)silane

and Methoxy polyethylene glycol 1,000

monomethacrylate

A solution was prepared by dissolving 7.1 g of

methoxy polyethylene glycol 1,000 monomethacrylate

in 100 ml of toluene. The solution was carefully

transferred to a 250 ml three-neck flask fitted with

a magnetic stirrer and a condenser. To this, 12.8 g

of

3-methacryloyloxypropyltris(trimethylsiloxy)silane

(TRIS), 1.0 g of distilled thioglycolic acid (TGA)

and 0.059 g of azobisisobutyronitrile (AIBN) were

added. AIBN was recrystallized from ethanol before

use. The solution was then deoxygenated using

nitrogen for 15 minutes and then placed under a

passive nitrogen blanket. After stirring for

16 hours at 60°C the percent conversion was

determined to be 95-98% by near infrared (NIR)

analysis. The number average molecular weight was

determined by size exclusion chromatography vs.

polystyrene and by end group titration. The Mn

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values were 2,895 and 2,083 respectively. The

polydispersity of the copolymer was 1.5.

EXAMPLES 12-17

Copolymerization of 1H,1H,5H

Octafluoropentylmethacrylate and Methoxy

polyethylene glycol monomethacrylates

Example 12

OFPMA, 15 g, methoxy polyethylene glycol 1,000

monomethacrylate, 50 g, 2-mercaptoethanol, 2.34 g,

and AIBN (recrystallized from ethanol), 0.164 g,

were combined with 500 mL of a 1:1 mixture of THF

and methanol(MEOH) in a 1 L, three-neck flask. The

flask was also fitted with a magnetic stirrer and a

reflux condenser. The mixture was stirred until all

reagents were in solution. A slow stream of

nitrogen was then used to deoxygenate the solution

for 15 minutes. After 72 hours of reflux under a

nitrogen atmosphere the conversion to copolymer was

99+% (by NIR analysis). Solvent was removed by

flash evaporation leaving a viscous oil, which upon

standing formed a wax-like solid. Values for Mn, Mw

and Pd were determined vs. polystyrene, (Mn= 3,700,

Mw= 6,300 and Pd= 1.72).   Results are shown in
Table II.

Examples 13-17

The procedure of Example 12 was repeated using
methoxy polyethylene glycol monomethacrylate in
different molecular weights and relative amounts as
indicated in Table II which also summarizes the
results obtained.

Table II

HYDROXY TERMINATED COPOLYMERS

Example #	Type	Composition	Conversion, % (by NIR)	time hrs	Mn	Mw	Pd
12	OFPMA/Peo 400	50/50	95	48	2190	3400	1.56
13	OFPMA/Peo 1k	50/50	99	72	3700	6300	1.72
14	OFPMA/Peo 5k	80/20	90	72	10.5k	16.1k	1.52
15	OFPMA/Peo 5k	50/50	75	65	10k	12.6k	1.27
16	OFPMA/Peo 2k	50/50	79	65	-	-	-
17	OFPMA/Peo 2k	80/20	95	48	3900	4800	1.22

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EXAMPLES 18-21

Surface Active Macromonomer Preparation

Example 18

Distilled glycidyl methacrylate, 1.83 g,

p-methoxyphenol, 2.5 mg (MEHQ), and two drops of

N,N-dimethyldodecylamine were added to the solution

from Example 7. The mixture was allowed to reflux

under a nitrogen atmosphere for 5 hours. The

solution was washed 3 times with dilute sodium

carbonate solution and once with water. The organic

layer was dried over magnesium sulfate, and toluene

removed by flash evaporation at reduced pressure.

The residue, 18.12 g (85% yield), of viscous yellow

macromonomer had Mn values of 3,353 (by SEC vs.

polystyrene) and 3,416 (by vapor phase

osmometry,vpo). The polydispersity (Pd) of the

macromonomer was 1.9. Results are summarized in

Table III.

Examples 19-21

The procedure of Example 18 was repeated using

the solutions from Examples 8-10. The copolymers of

Examples 9-10 were isolated and redissolved in
dioxane for surface active macromonomer preparation.
Results obtained are shown in Table III.

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Table III

SURFACE ACTIVE MACROMERS

Example #	Type	Composition	Solvent	Rxn time	Mn	Mn	Pd
18	OFPMA/Peo 1k	80/20	Toluene	5h	3353	6493	1.9
19	OFPMA/Peo 1k	70/30	Toluene	5h	2057	4587	2.2
20	OFPMA/Peo 1k	50/50	Dioxane	5h	2545	4351	1.7
21	OFPMA/Peo 5k	80/20	Dioxane	5h	8142	12k	1.5

EXAMPLES 22-27

Surface Active Macromonomer Preparation

Example 22

Hydroxy terminated copolymer, 41.744 g (from Example 12), was dissolved in 225 mL of THF, in a 500 mL 3-neck flask fitted with a magnetic stirrer, a reflux condenser, and an addition funnel. Dibutyltin dilaurate, 1.57 g, and butylated hydroxy toluene, 10 mg, were added. Isocyanatoethyl methacrylate, 1.98 g (ICEM) in 25 mL $CHCl_3$, was added dropwise. Following the addition the solution was heated to reflux. After 16 hours 0.2% ICEM was detected by infrared analysis. Methanol, 5 mL, was added to react with the slight excess of ICEM. Chloroform was then removed by flash evaporation. The residue was left under high vacuum overnight to remove residual solvent leaving 42.4 g of wax-like semisolid. Values for the Mn, Mw, and Pd were determined vs polystyrene standards. Results are summarized in Table IV.

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Examples 23-27

The procedure of Example 22 was repeated using hydroxy terminated copolymers (dissolved in chloroform) from Examples 13-17. Results are shown in Table IV.

Table IV

SURFACE ACTIVE MACROMERS

Example #	Type	Composition	Solvent	Time hrs	Mn	Mn	Pd
22	OFPMA/Peo 400	50/50	THF	16	2500	4600	1.8
23	OFPMA/Peo 1k	50/50	CHCl$_3$	16	4000	6700	1.69
24	OFPMA/Peo 5k	80/20	CHCl$_3$	12	4100	4500	1.12
25	OFPMA/Peo 5k	50/50	CHCl$_3$	16	9900	12.5K	1.26
26	OFPMA/Peo 2k	50/50	CHCl$_3$	16	-	-	-
27	OFPMA/Peo 2k	80/20	CHCl$_3$	16	3800	4500	1.19

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EXAMPLE 28

Surface Active Macromonomer Preparation

Distilled glycidyl methacrylate, 1.58 g,
p-methoxyphenol, 2.8 mg (MEHQ), and two drops of
N,N-dimethyldodecylamine were added to the solution
from Example 11. The mixture was allowed to reflux
under a nitrogen atmosphere for 5 hours. The
solution was washed 3 times with dilute sodium
carbonate solution and once with water. The organic
layer was dried over magnesium sulfate, and toluene
was removed by flash evaporation at reduced
pressure. The residue, 17.64 g (84% yield), of
viscous semi-solid macromonomer had Mn values of
1,593 (by SEC vs. polystyrene) and 1,918 (by vapor
phase osmometry,vpo). The polydispersity of the
macromonomer was 1.6.

EXAMPLE 29

Surface Active Macromonomer Preparation

Hydroxy terminated copolymer, 3.14 g (from
Example 3), was dissolved in 90 mL of chloroform, in

a 250 mL 3-neck flask fitted with a magnetic

stirrer, a reflux condenser, and an addition funnel.

Dibutyltin dilaurate, 3 drops and butylated hydroxy

toluene, 3 mg, were added. Isocyanatoethyl

methacrylate, 89 uL (ICEM) in 10 mL $CHCl_3$, was added

dropwise. Following the addition the solution was

heated to reflux. After 12.5 hours no ICEM could be

detected by infrared analysis. The reaction mixture

was then slowly added to 2 L of anhydrous ethyl

ether and the solid collected. After drying at 30°C

under reduced pressure the yield of macromer was

3 g. The Mn, Mw and Pd values were 4,900, 5,900 and

1.2 (vs. polyethylene glycol standards).

EXAMPLE 30

Surface Active Macromonomer Preparation

Hydroxy terminated copolymer, 4.5 g, (from

Example 6) was dissolved in 90 mL of chloroform in a

250 mL 3-neck flask fitted with a magnetic stirrer,

a reflux condenser, and an addition funnel.

Dibutyltin dilaurate, 2 drops and butylated hydroxy

toluene, 3 mg, were added. Isocyanatoethyl

methacrylate, 93 uL (ICEM) in 10 mL $CHCl_3$, was added

dropwise. Following the addition the solution was
heated to reflux. After 20 hours a trace of ICEM
could be detected by infrared analysis. The
reaction mixture was then slowly added to 2 L of
anhydrous ethyl ether and the solid collected.
After drying at 30°C under reduced pressure the
yield of macromer was 3.14 g. The Mn, Mw and Pd
values were 4,900, 8,900 and 1.8 (vs. PEG
standards).

EXAMPLES 31-42

Surface Tension Determination Using
the Wilhelmy Plate Technique

Macromonomer solutions were prepared with
distilled water at molar concentrations of
10^{-2}-10^{-6}. The surface tension of each solution was
measured by the Wilhelmy Plate technique on a
Wettek, model SFA-212, instrument. A test solution
was placed in a jacketed beaker, which had been
cleaned with chromic/sulfuric acid for 40 minutes,
rinsed with clean water and dried overnite at 120°C.
Data was collected by dipping a glass cover slip

(cleaned by passing through a flame) into each
solution several times at the following conditions:

Platform speed	0.16 mm/sec
Immersion depth	20.0 mm
Temperature	34 ± 1°C

The data was analyzed using WETTEK 12 software.
Results are shown below in Table V.

Table V

SURFACE TENSION DATA

Example #	Macromer example #	Molar conc.	Temp. C	Surface Tension dyne/cm
31	7	10^{-2}	34	32.3
32	7	10^{-3}	34	34.8
33	7	10^{-4}	34	46.8
34	5	10^{-3}	23	36.3
35	5	10^{-4}	23	46.2
36	5	10^{-5}	23	57.5
37	5	10^{-6}	23	66.8
38	6	10^{-2}	23	31.8
39	6	10^{-3}	23	34.3
40	6	10^{-4}	23	38.7
41	6	10^{-5}	23	53.1
42	6	10^{-6}	23	65.9

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EXAMPLE 43

Polyurethane Monomer Mix

A urethane prepolymer prepared from isophorone diisocyanate, diethylene glycol, polysiloxanediol (molecular wt. 3,000) and endcapped with 2-hydroxyethyl methacrylate was combined with the following; methacryloyloxypropyl tris(trimethylsiloxy)silane (TRIS), N,N-dimethylacrylamide (DMA), N-hexanol, benzoin methyl ether (BME). The proportions are given below.

Urethane prepolymer	35 parts
TRIS	35 parts
DMA	30 parts
N-hexanol	40 parts
BME	0.2 parts

The resulting clear mix was then filtered through a 1.2 micron filter into a clean glass vial.

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EXAMPLE 44

Polyurethane Monomer Mix Containing
Surface Active Macromer (SAM)

A monomer mix was prepared as in Example 43 except that 0.25 parts by weight of SAM 80/20 (Example 18) was added.

EXAMPLE 45

Polyurethane Monomer Mix Containing SAM

A monomer mix was prepared as in Example 43 except that 0.25 parts by weight of SAM 50/50 (Example 20) was added.

EXAMPLE 46

Polyurethane Monomer Mix Containing SAM

A monomer mix was prepared as in Example 43 except that 0.25 parts by weight of SAM 80/20 5k (Example 23) was added.

EXAMPLE 47

Polyurethane Monomer Mix Containing SAM

A monomer mix was prepared as in Example 43 except that 0.25 parts by weight of SAM (Example 29) was added.

EXAMPLE 48

Polyurethane Monomer Mix Containing SAM

A monomer mix was prepared as in Example 30 except that 0.25 parts by weight of SAM (Example 30) was added.

EXAMPLE 49

Vinyl Carbonate Monomer Mix

A solution was prepared by combining
3[tris(trimethylsiloxy)silyl]propyl vinyl

carboxamide (TRISV), 1-vinyl-2-pyrrolidinone

(NVP),pentacontamethyl-a,w-bis

(4-vinyloxycarbonyloxybutyl)pentacosa siloxane

(V2D25, Mw range 2-4k), nonanol, and

2-hydroxy-2-methyl-1-phenylpropan-1-one (DarocurR).

The proportions (by weight) are listed below.

TRISV	55 parts
NVP	30 parts
V2D25	15 parts
Nonanol	10 parts
DarocurR	0.2 parts

The solution was filtered into a glass vial.

EXAMPLE 50

Vinyl Carbonate Monomer Mix Containing SAM

A monomer mix was prepared as in Example 49

except that 0.36 parts by weight of SAM 80/20 5k

(Example 24) was added.

EXAMPLE 51

Fluorosilicone Prepolymer Mix

Dimethacrylate-capped polydimethylsiloxane/polymethyl-trifluoropropylsiloxane $M_2D_{35}F_{65}$ as described in U.S. Patent 4,810,764 (fluorosilicone), octafluoropentylmethacrylate (OFPMA), 2-vinyl-4,4-dimethyl-2-oxazalin-5-one (VDMO), and benzoin methyl ether (BME) were combined in the weight proportions shown below.

Fluorosilicone	98 parts
OFPMA	2 parts
VDMO	5 parts
BME	0.2 parts

The resulting solution was filtered. The fluorosilicone monomer employed is described by the formula

$$A(CH_2)_4 \underset{R^2}{\overset{R^1}{\underset{|}{\overset{|}{\underset{Si}{-}}}}} - O \Bigg]_m \left[\underset{R^4}{\overset{R^3}{\underset{|}{\overset{|}{\underset{Si}{-}}}}} - O \right]_n \underset{R^2}{\overset{R^1}{\underset{|}{\overset{|}{\underset{Si}{-}}}}} - (CH_2)_4 - A$$

wherein A is a methacrylate group; R_1, R_2 and R_3 are methyl groups; R_4 is a trifluoropropyl group; m is 36; and n is 65.

EXAMPLE 52

Fluorosilicone Prepolymer Mix Containing SAM

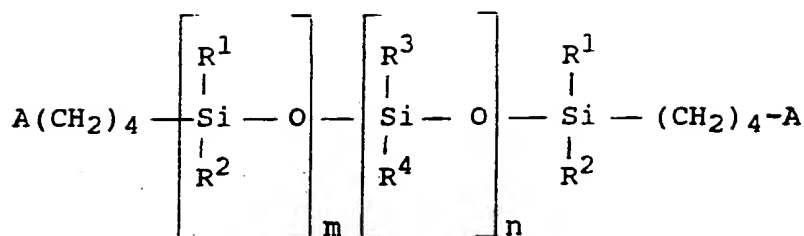A monomer mix was prepared as in Example 51 except that 0.25 parts by weight of SAM 80/20 5k (Example 24) was added.

EXAMPLE 53

Fluorosilicone Prepolymer Mix Containing SAM

A monomer mix was prepared as in Example 51 except that VDMO was replaced with SAM 80/20 5k (Example 24).

EXAMPLE 54-64

Contact Lens Cast Molding

Anterior and posterior mold surfaces were
cleaned by electrostatic deionization in air and
transferred to an inert (nitrogen) atmosphere. The
mold anterior was then filled with 40-80 uL of
monomer mix, (examples 43-53) in the inert
atmosphere and placed on a casting plate. The mold
posterior was then positioned. Once the casting
plate was full the top plate was aligned and
tightened down to 18 inch-pounds. Casting plates
were then placed under ultraviolet light at 4,000 u
watts/cm^2,(oxygen level was <50ppm), for one hour.
Following separation the mold halves containing
lenses were placed in a 70/30 volume/volume solution
of ethanol and water or 100% ethanol. Lenses and
solution were placed in an ultrasonic bath at 50°C
and allowed to release. Lenses were then
transferred to absolute ethanol. After one hour the
solvent was exchanged with fresh ethanol and allowed
to stand for 48 hours. Ethanol was then removed by
water extraction.

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EXAMPLE 65

Analysis for Surface-Active Macromer at Contact Lens

Surface Electron spectroscopy for chemical analysis

(ESCA)

Electron spectroscopy for chemical analysis
(ESCA) utilizes a monochromatic source of low energy
x-ray to produce a core level ionization. The
energies of the ejected photons are measured and
subtracted from that of the incident photon to
obtain their binding energies. These energies
identify the elements present at or near the sample
surface.

The polyurethane lens of Example 55 was
subjected to ESCA analysis at x-ray incident angles
of 15, 45, and 90 degrees. The smaller the incident
angle, the shallower the probe depth of the sample
surface. The atomic percent concentration of
fluorine at the different incident angles was 5.33,
3.38 and 3.33%, respectively. These data for the
fluorine atom are indicative of a high concentration
of surface-active macromer at the lens surface

because the concentration of total macromer in the

lens sample was only 0.25 weight %.

EXAMPLE 66

Analysis for Surface-Active Macromer at Contact Lens

Surface Contact Angle

The contact angle of the surface of contact

lenses prepared in Examples 54, 55, 56, and 58 were

measured by the captive bubble technique. The

lenses were submerged in buffered saline solution

and a bubble of air was attached to the undersurface

of the lens. The angle made by the intersection of

the lens and bubble surfaces was measured using a

goniometer. The lower the contact angle the more

hydrophilic or water wettable is the lens surface.

Results are shown in Table VI. Note that the lens

of Example 54 contained no polymerizable surfactant.

Addition of polymerizable surfactant as in

Examples 55, 56, and 58 caused a marked reduction in

the contact angle.

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Table VI

Example No.	Contact Angle
54	35
55	20
56	14
58	24

EXAMPLE 67

Clinical Evaluation of Example 57

Five subjects wore one contact lens of Example
57 (containing the polymerizable surfactant of
Example 23) in one eye and one control contact lens,
Example 54 (without polymerizable surfactant) in the
other eye. The lenses were analyzed after a minimum
of one hour of wear for surface characteristics of
wettability and surface deposition. The wettability
rating scale was 0-4, where 0 was more than 2/3 of
the anterior lens surface unwetted by tear film and
4 represented complete (100%) wetting by tear film.
The deposition scale was 0-4 where 0 represented no
surface deposits and 4 was multiple deposits of

0.5 mm diameter or larger. The results for the
lenses of Example 57 were wettability 3.2 and
deposits 1.0 compared to 2.0 and 1.6, respectively,
for the control lenses of Example 54.

EXAMPLE 68

Clinical Evaluation of Example 61

Six subjects wore contact lenses of Example 61
(prepared from the monomer mix of Example 50 and
containing the polymerizable surfactant of
Example 24) in both eyes for a period of one hour
and the lenses were analyzed as in Example 67. The
results were wettability 3.2 and deposits 0.1 which
compares favorably to values of 2.0 and 1.6,
respectively for wettability and deposits for
control lenses of Example 54 (which contained no
polymerizable surfactant).

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EXAMPLE 69

Clinical Evaluation of Example 56 (1K 50/50 PEOSAM)

Eight subjects wore one contact lens of Example
56 (prepared from the monomer mix of Example 45 and
containing the polymerizable surfactant of
Example 20) and one control contact lens, Example 54
(without polymerizable surfactant), in the other
eye. The lenses were analyzed as in Example 67
after a minimum of one hour of wear for surface
characteristics of wettability and surface
deposition. The results for the lenses of
Example 56 were wettability 2.6 and deposits 1.2
which compares favorably to values of 2.1 and 1.7,
respectively, for wettability and deposits for
control lenses of Example 54.

EXAMPLE 70

Clinical Evaluation of Example 58 (80/20 NVPSAM)

Five subjects wore contact lenses of Example 58
(prepared from the monomer mix of Example 47 and
containing the polymerizable surfactant of

Example 29) for a period of one hour and the lenses
were analyzed as in Example 67. The results were
wettability 2.6 and deposits 1.4 which compares
favorably to values of 2.0 and 1.6, respectively for
wettability and deposits for control lenses of
Example 54.

EXAMPLE 71

Surface Coating of Polyurethane Contact Lenses

A solution of 0.1 mmol surface-active macromer
of Example 18, 0.007 g of neopentyl glycol
dimethacrylate and 0.0038 g of BME in 100 mL of
deoxygenated, distilled water was prepared by
stirring at room temperature for one hour. One
contact lens, prepared as described in Example 54,
was placed in a 10 mL lens vial and the vial was
filled with the solution under a nitrogen atmosphere
in a glove box. The vial was sealed with a Teflon
lined stopper and crimp seal, placed on its side and
irradiated with 2500 uW/cm^2 of UV light for 2 hours.
The lens was removed from the vial, washed with
distilled water, extracted in ethanol for 2 hours
and boiled in distilled water for 2.5 hours. The

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lens was then sealed in a vial in buffered saline
solution.

EXAMPLE 72

Surface Coating of Polyurethane Contact Lenses

A solution of 0.1 mmol surface-active macromer
of Example 20, 0.01 g of neopentyl glycol
dimethacrylate and 0.003 g of BME in 100 mL of
deoxygenated, distilled water was prepared by
stirring at room temperature for one hour. One
contact lens, prepared as described in Example 54,
was placed in a 10 mL lens vial and the vial was
filled with the solution under a nitrogen atmosphere
in a glove box. The vial was sealed with a Teflon
lined stopper and crimp seal, placed on its side and
irradiated with 2500 uW/cm^2 of UV light for 2 hours.
The lens was removed from the vial, washed with
distilled water, extracted in ethanol for 2 hours
and boiled in distilled water for 2.5 hours. The
lens was then sealed in a vial in buffered saline
solution.

EXAMPLE 73

Surface Coating of Silicone (SIL-TECH) Contact
Lenses

A solution of 0.1 mmol surface-active macromer
of Example 18, 0.007 g of neopentyl glycol
dimethacrylate and 0.003 g of BME in 100 mL of
deoxygenated, distilled water was prepared by
stirring at room temperature for one hour. A SIL-
TECH silicone elastomer contact lens (available from
Bausch & Lomb Incorporated) was placed in a 10 mL
lens vial and the vial was filled with the solution
under a nitrogen atmosphere in a glove box. The
vial was sealed with a Teflon lined stopper and
crimp seal, placed on its side and irradiated with
2500 uW/cm^2 of UV light for 2 hours. The lens was
removed from the vial, washed with distilled water,
extracted in 1:1 ethanol:isopropanol for 3 hours.
The lens was then sealed in a vial in buffered
saline solution.

EXAMPLE 74

Analysis for Surface-Active Macromer at Contact Lens

Surface

Contact Angle

The contact angle of the surface coated lenses
of Example 73 was measured and compared to an
untreated lens (control). The average contact angle
of three coated lenses was 38° versus 46° for the
control sample.

EXAMPLE 75

Clinical Evaluation of Example 71

Five subjects wore one contact lens of
Example 71 and one control contact lens (the
uncoated lens of Example 54, without post treatment)
in the other eye. The lenses were analyzed after
one hour of wear for surface characteristics of
wettability and surface deposition as in Example 67.
The results were wettability 2.8 and deposits 1.2
which compares favorably to values of 1.0 and 1.8,
respectively for wettability and deposits for
control lenses of Example 54.

What is claimed is:

1.   A random copolymer prepared by copolymerizing
at least one ethylenically unsaturated hydrophilic
monomer and at least one ethylenically unsaturated
hydrophobic monomer in the presence of a functional
chain transfer agent.

2.   A random copolymer described by the formula:

$$C[A_xB_y]$$

wherein A is at least one ethylenically unsaturated
hydrophilic monomer, B is at least one ethylenically
unsaturated hydrophobic monomer, C is a functional
chain transfer agent, y is within the range from
about 0.1 to about 0.9, and x + y = 1.

3.   The copolymer of claim 2 wherein the
ethylenically unsaturated hydrophilic monomer, A, is
selected from the group consisting of ethylenically
unsaturated polyoxyalkylenes, polyacrylamides,
polyvinylpyrrolidones, polyvinyl alcohols, poly
(HEMA), and N-alkyl-N-vinyl acetamide.

4.   The copolymer of claim 3 wherein the
ethylenically unsaturated hydrophilic monomer, A, is
an ethylenically unsaturated polyoxyalkylene
selected from the group consisting of
(meth)acrylated polyoxyalkylenes, (meth)acrylamido
polyoxyalkylenes, styrenyl polyoxyalkylenes, alkenyl
polyoxyalkylenes, vinyl carbonate polyoxyalkylenes
and vinyl carbamate polyoxyalkylenes.

5.   The copolymer of claim 4 wherein the
polyoxyalkylene is polyethylene oxide.

6.   The copolymer of claim 4 wherein the
ethylenically unsaturated hydrophilic monomer, A, is
(meth)acrylated polyethylene oxide.

7.   The copolymer of claim 4 wherein the
ethylenically unsaturated hydrophilic monomer, A, is
a methacrylate endcapped poly-N-vinylpyrrolidinone.

8.   The copolymer of claim 4 wherein the
ethylenically unsaturated hydrophilic monomer, A, is
a methacrylate endcapped poly-N,N-
dimethylacrylamide.

9.   The copolymer of claim 2 wherein the
ethylenically unsaturated hydrophobic monomer, B, is
selected from the group consisting of alkyl

(meth)acrylates, N-alkyl (meth)acrylamides, alkyl
vinylcarbonates, alkyl vinylcarbamates, fluoroalkyl
(meth)acrylates, N-fluoroalkyl (meth)acrylamides, N-
fluoroalkyl vinylcarbonates, N-fluoroalkyl
vinylcarbamates, silicone-containing
(meth)acrylates, (meth)acrylamides, vinyl
carbonates, vinyl carbamates, styrenic monomers and
polyoxypropylene (meth)acrylates.

10.   The copolymer of claim 9 wherein the styrenic
monomers are selected from the group consisting of
styrene, alpha-methyl styrene, para-methyl styrene,
para-t-butyl monochloro styrene, and para-t-butyl
dichloro styrene.

11.   The copolymer of claim 2 wherein the
ethylenically unsaturated hydrophobic monomer, B, is
TRIS.

12.   The copolymer of claim 2 wherein the
ethylenically unsaturated hydrophobic monomer, B, is
1-H,1-H,5-H-octafluoropentyl methacrylate.

13.   The copolymer of claim 2 wherein the functional
chain transfer agent, C, is selected from the group
consisting of mercapto carboxylic acids, mercapto
alcohols, and aminomercaptans.

14. The copolymer of claim 2 wherein the functional chain transfer agent, C, is thioglycolic acid.

15. The copolymer of claim 2 wherein the functional chain transfer agent, C, is 2-mercaptoethanol.

16. The copolymer of claim 2 wherein the functional chain transfer agent, C, is 2-aminoethane thiol.

17. A surface-active macromer described by the formula:

$$DC[A_xB_y]$$

wherein A is at least one ethylenically unsaturated hydrophilic monomer, B is at least one ethylenically unsaturated hydrophobic monomer, C is a functional chain transfer agent, and D is an ethylenically unsaturated end group.

18. The surface-active macromer of claim 17 wherein A is selected from the group consisting of ethylenically unsaturated polyoxyalkylenes, polyacrylamides, polyvinylpyrrolidones, polyvinyl alcohols, poly (HEMA), and N-alkyl-N-vinyl acetamide.

19. The surface-active macromer of claim 17 wherein A is an ethylenically unsaturated polyoxyalkylene selected from the group consisting of

(meth)acrylated polyoxyalkylenes, (meth)acrylamido
polyoxyalkylenes, styrenyl polyoxyalkylenes, alkenyl
polyoxyalkylenes, vinyl carbonate polyoxyalkylenes
and vinyl carbamate polyoxyalkylenes.

20.   The surface-active macromer of claim 19 wherein
the polyoxyalkylene is polyethylene oxide.

21.   The surface-active macromer of claim 17 wherein
A is (meth)acrylated polyethylene oxide.

22.   The surface-active macromer of claim 17 wherein
A is a methacrylate endcapped poly-N-
vinylpyrrolidinone.

23.   The surface-active macromer of claim 17 wherein
A is a methacrylate endcapped poly-N,N-
dimethylacrylamide.

24.   The surface-active macromer of claim 17 wherein
B is selected from the group consisting of alkyl
(meth)acrylates, N-alkyl (meth)acrylamides, alkyl
vinylcarbonates, alkyl vinylcarbamates, fluoroalkyl
(meth)acrylates, N-fluoroalkyl (meth)acrylamides, N-
fluoroalkyl vinylcarbonates, N-fluoroalkyl
vinylcarbamates, silicone-containing
(meth)acrylates, (meth)acrylamides, vinyl
carbonates, vinyl carbamates, styrenic monomers and
polyoxypropylene (meth)acrylates.

25. The surface-active macromer of claim 24 wherein
the styrenic monomers are selected from the group
consisting of styrene, alpha-methyl styrene, para-
methyl styrene, para-t-butyl monochloro styrene, and
para-t-butyl dichloro styrene.

26. The surface-active macromer of claim 17 wherein
B is 1-H,1-H,5-H-octafluoropentyl methacrylate.

27. The surface-active macromer of claim 17 wherein
C is selected from the group consisting of mercapto
carboxylic acids, mercapto alcohols, and
aminomercaptans.

28. The surface-active macromer of claim 17 wherein
C is thioglycolic acid.

29. The surface-active macromer of claim 17 wherein
C is 2-mercaptoethanol.

30. The surface-active macromer of claim 17 wherein
C is 2-aminoethane thiol.

31. The surface-active macromer of claim 28 wherein
D is a (meth)acrylated hydroxy ester moiety derived
from glycidyl (meth)acrylate.

32. The surface-active macromer of claim 29 wherein
D is a (meth)acrylated ester moiety derived from
(meth)acryloyl chloride.

33. The surface-active macromer of claim 29 wherein
D is a (meth)acrylated urethane moiety derived from
(meth)acrylated isocyanate.

34. The surface-active macromer of claim 29 wherein
D is a vinylcarbonate derived from vinyl
chloroformate.

35. The surface-active macromer of claim 30 wherein
D is a (meth)acrylated amide moiety derived from
(meth)acryloyl chloride.

36. The surface-active macromer of claim 30 wherein
D is a (meth)acrylated urea moiety derived from
(meth)acrylated isocyanate.

37. The surface-active macromer of claim 30 wherein
D is a vinyl carbamate moiety derived from vinyl
chloroformate.